EPA/States Corrective Action Workshop
Cacapon Resort State Park

Mike Liberati - DuPont Corporate Remediation Group

Zero-Valent Iron
Source Treatment Technology

AKA
SATURATION BOMBING

Topics to be Covered

- Background on Zero-Valent Iron
- Field Demonstration of ZVI Source Treatment
- Application at the DuPont Martinsville, VA site

Zero-Valent Metals

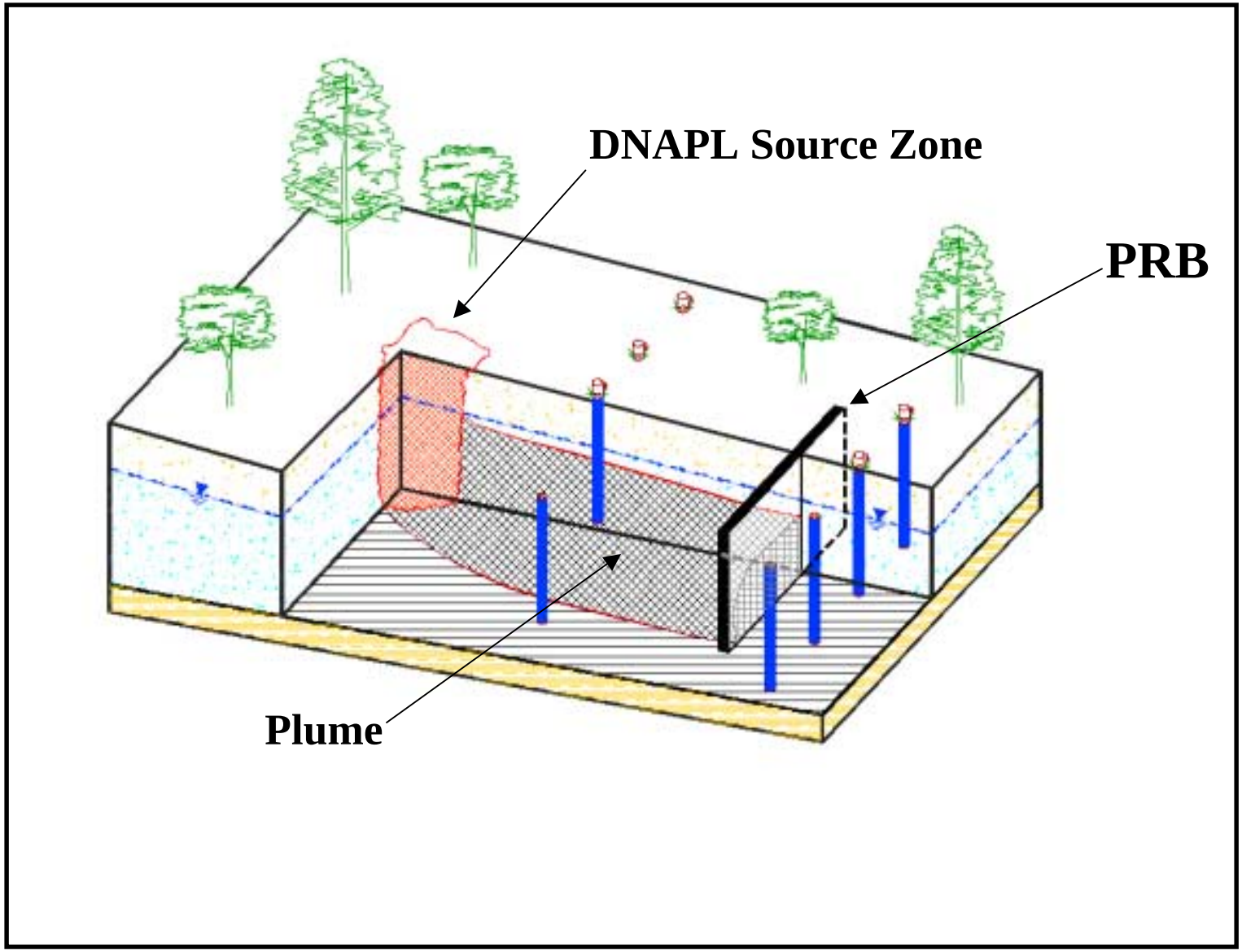
- Promote degradation of chlorinated organic compounds
- Promote precipitation of redox sensitive trace metals, radionuclides
- Focus on zero-valent iron [Fe^0] to treat groundwater affected by:
  - chlorinated ethenes
  - chlorinated ethanes
  - chlorinated methanes (some)
  - dissolved metals

Permeable Reactive Barrier (PRB)

- A permeable zone containing or creating a reactive treatment area oriented to intercept and remediate a contaminant plume
- Removes contaminants from the groundwater flow system by physical, chemical, or biological processes

A PRB for Horizontal Flow

PRB Cut-away Diagram



Treatment Processes

- pH control
- Chemical precipitation
- Oxidation-reduction reactions
- Zero-valent metal dehalogenation
- Biological degradation reactions
- Sorption reactions
  - sorption of organics
  - sorption of inorganics

Emplacement Methods

- Conventional excavation
- Trenching machine
- Deep soil mixing
- High-pressure jetting
- Vertical hydraulic fracturing (hydrofracturing)

Reaction Mechanism - VOCs

- Corrosion of iron drives reaction
- Iron provides electron source for reduction (dechlorination) of organics

Reaction Summary—cVOCs

$$Fe^{0} \longrightarrow Fe^{+2} + 2e^{-}$$

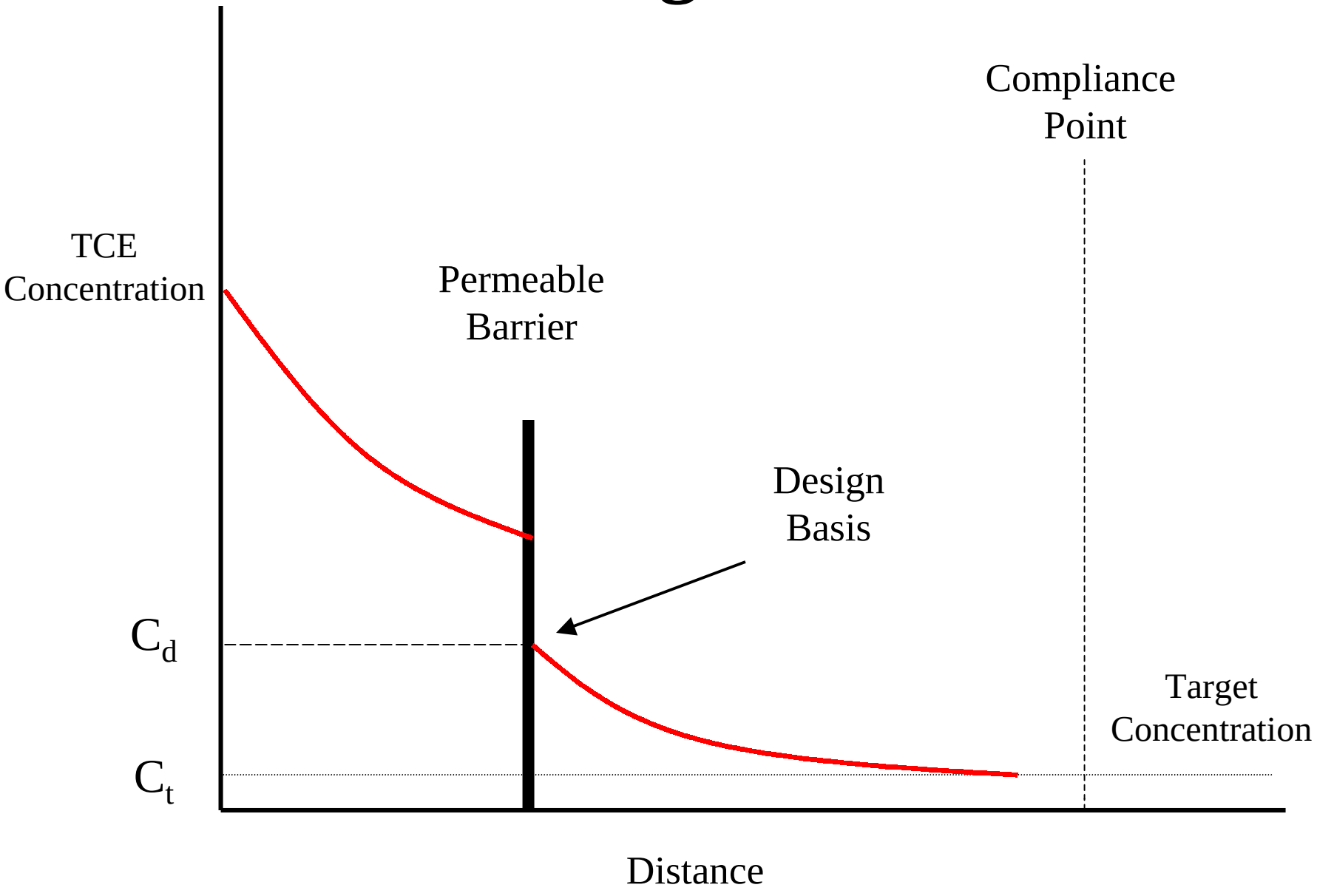
$$2H_2O \longrightarrow 2H^{+} + 2OH^{-}$$

$$2H^{+} + 2e^{-} \longrightarrow H_{2(g)}$$

$$X\text{-}Cl + H^{+} + 2e^{-} \longrightarrow X\text{-}H + Cl^{-}$$

$$C_2HCl_3 + 3H^{+} + 6e^{-} \longrightarrow C_2H_4 + 3Cl^{-}$$

TCE Degradation



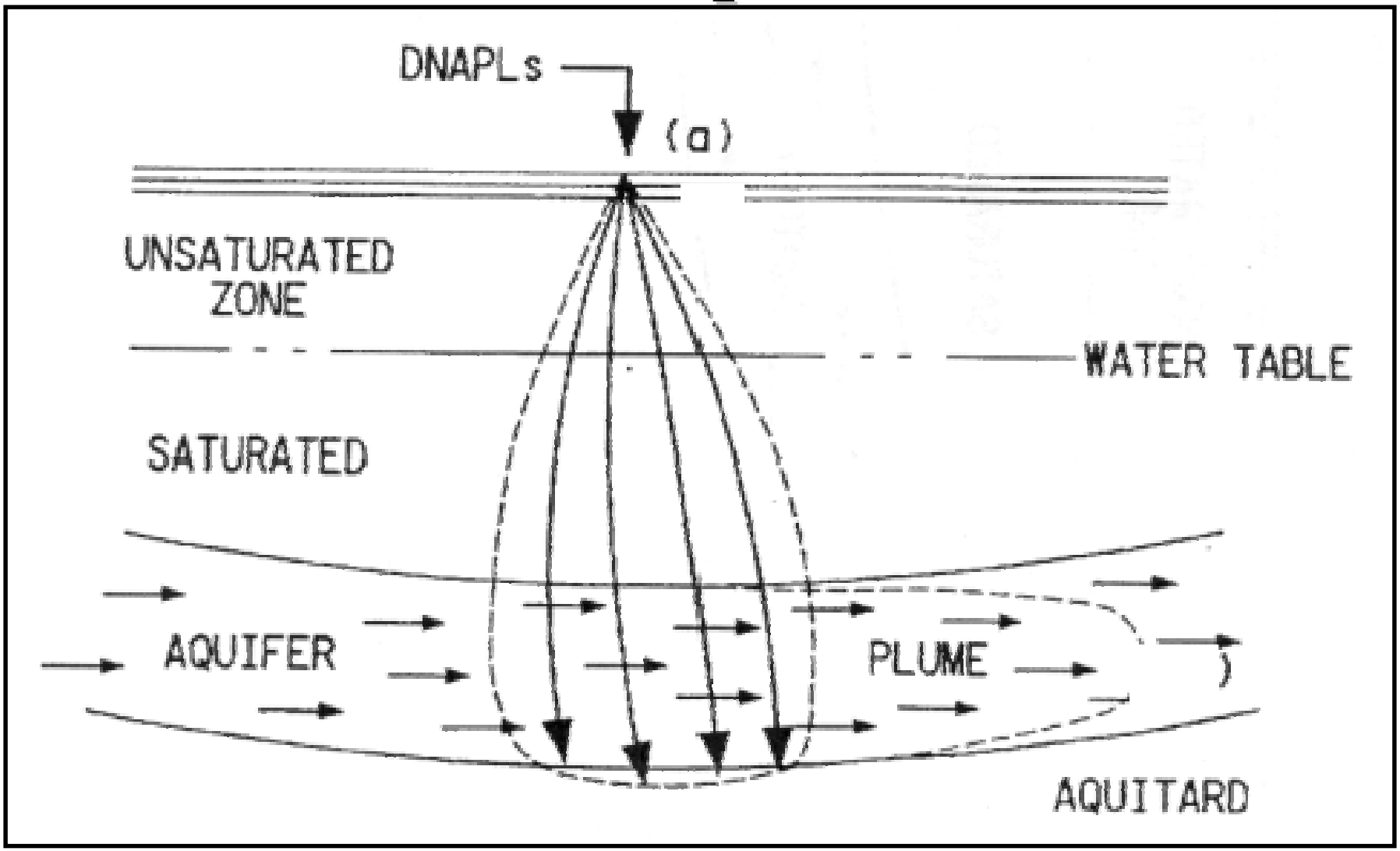
Compounds Treated By ZVI

Organic Compounds			
Methanes	• tetrachloromethane • trichloromethane	Propanes	• 1,2,3-trichloropropane • 1,2-dichloropropane
Ethanes	• hexachloroethane • 1,1,1-trichloroethane • 1,1,2-trichloroethane • 1,1-dichloroethane	Other	• hexachlorobutadiene • 1,2-dibromoethane (EDB) • freon 113 • freon 11 • lindane • N-nitrosodimethylamine • nitrobenzene
Ethenes	• tetrachloroethene • trichloroethene • cis-1,2-dichloroethene • trans-1,2-dichloroethene • 1,1-dichloroethene • vinyl chloride		

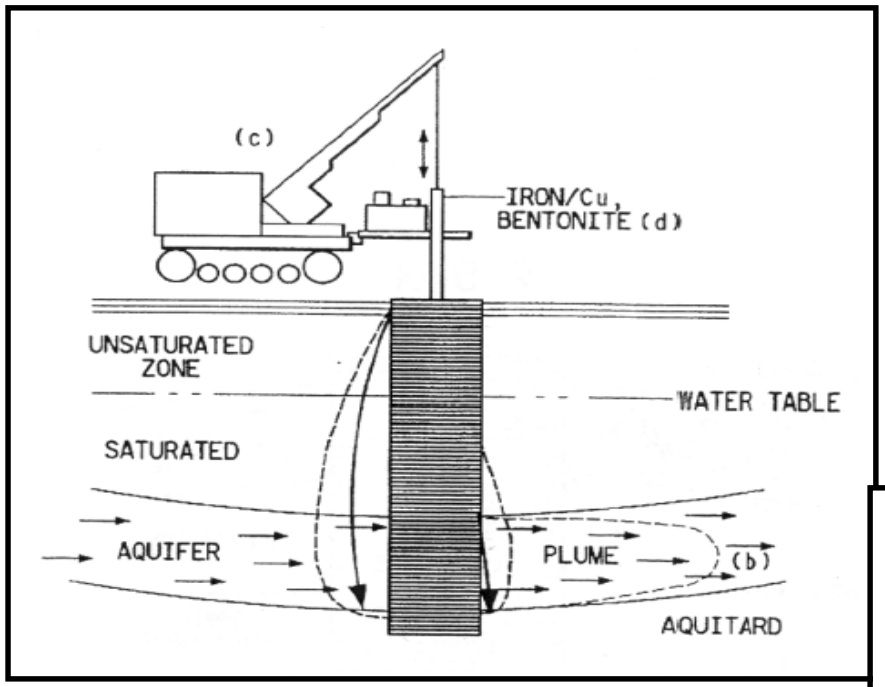
Typical Half-Lives

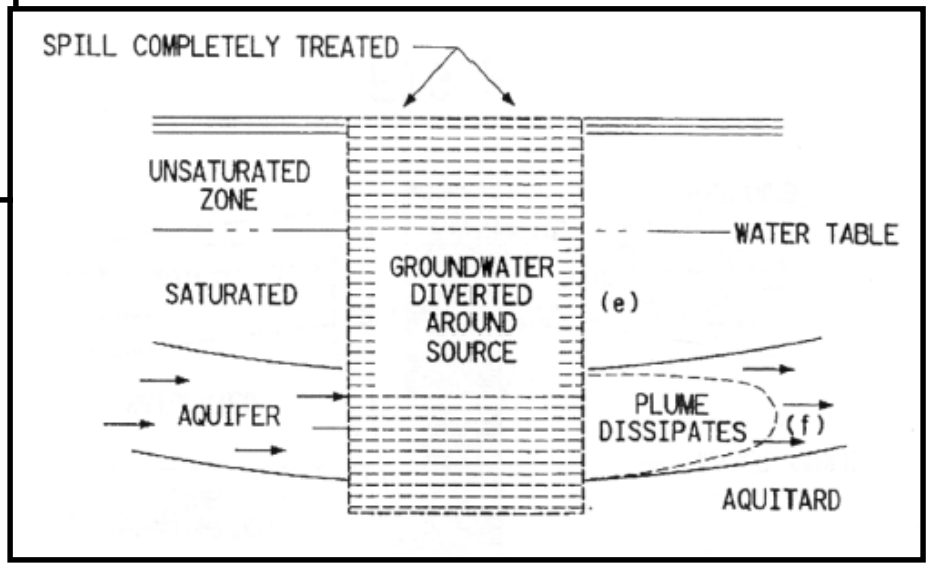
Compound	*Typical Half-Life (hours)*	*Compound*	*Typical Half-Life (hours)*
PCE	**0.5-2**	**CT**	**0.5-1**
TCE	**0.5-2**	**TCM**	**1-3**
***cis* 1,2-DCE**	**2-6**	**1,1,1-TCA**	**0.5-2**
VC	**2-6**	**1,1-DCA**	**10-24**

Problem Definition
DNAPL Spill Zone



Zero Valent Iron Source Treatment

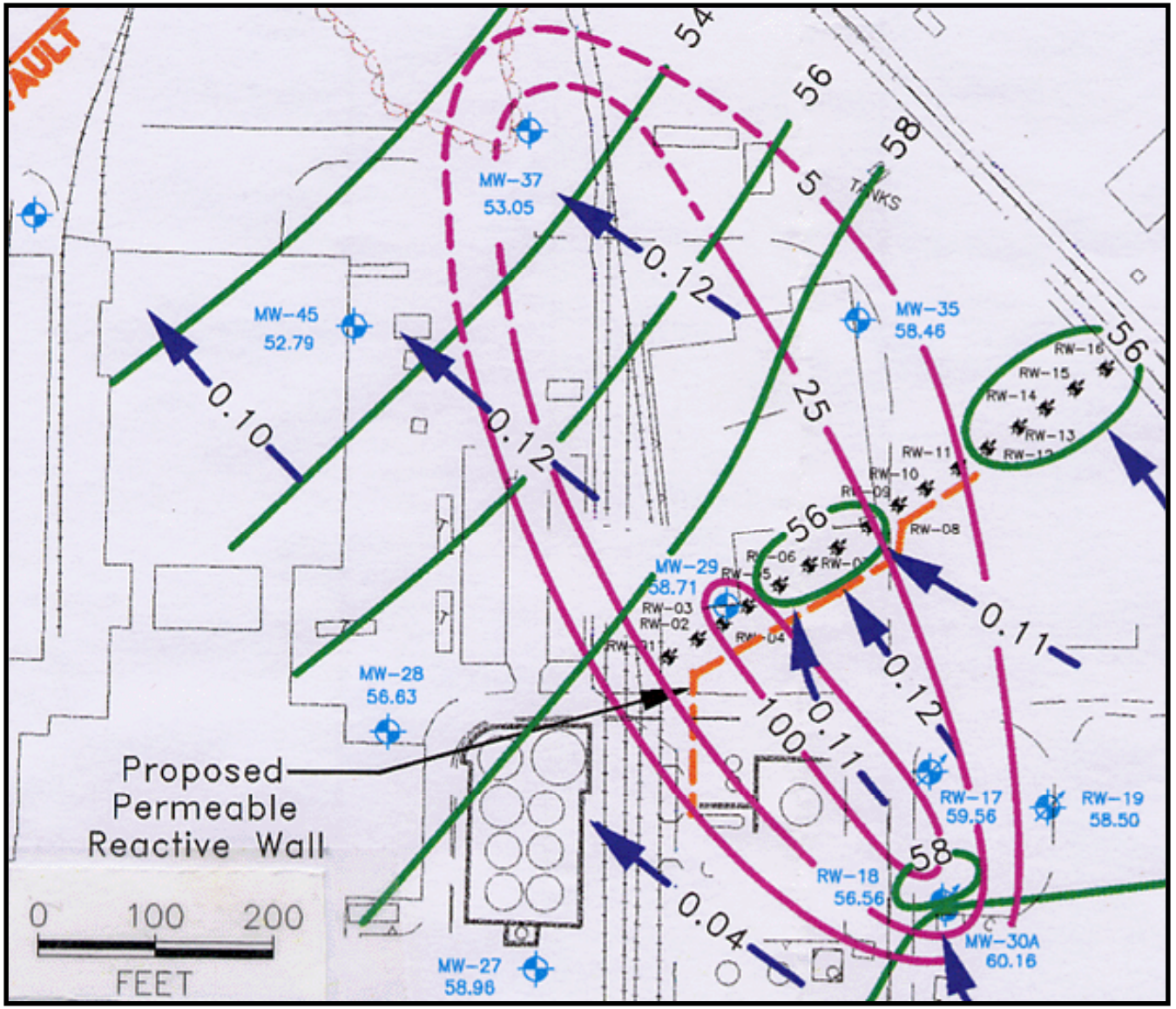




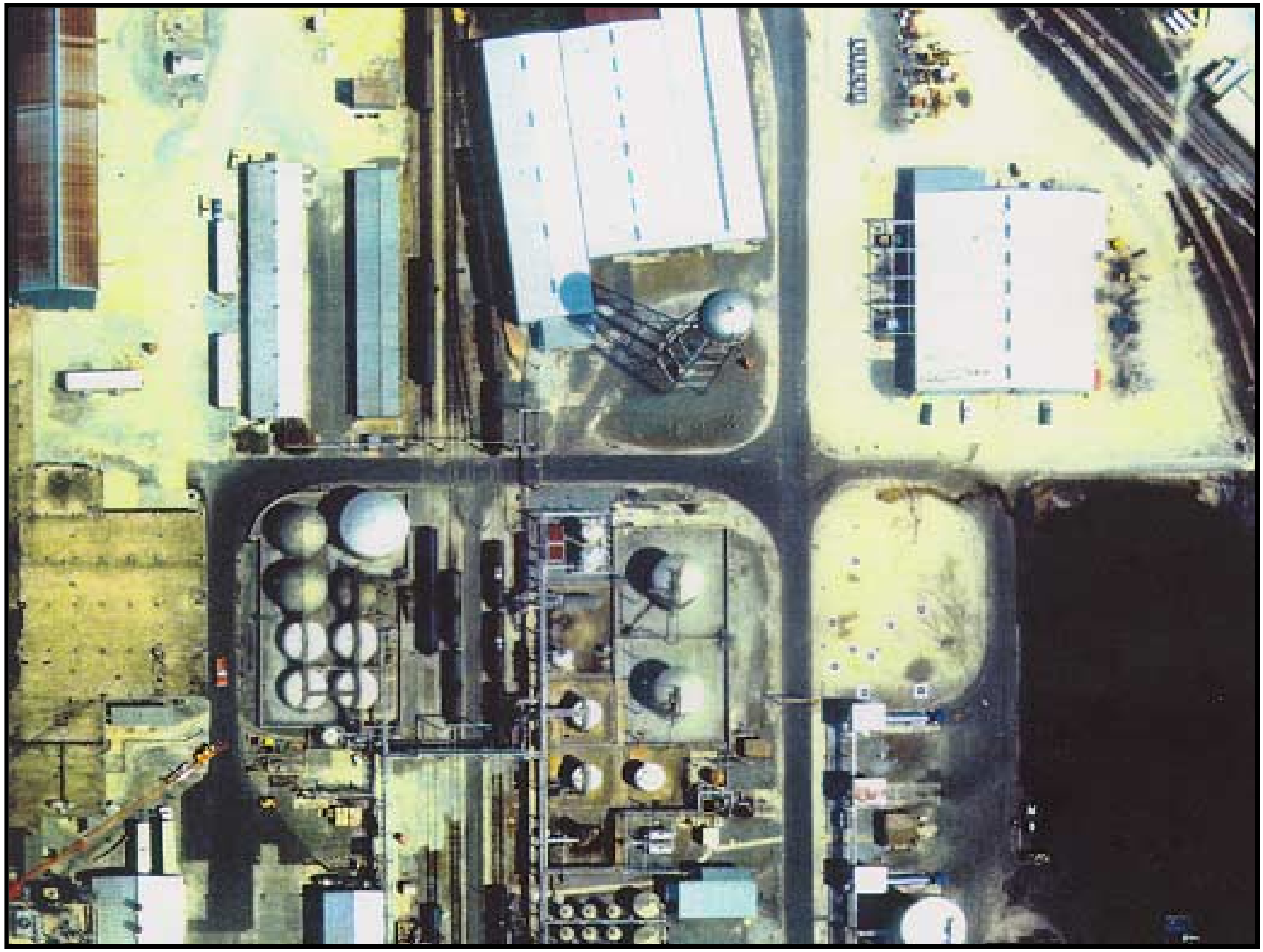
Deep Soil Mixing Augers

Courtesy of SWM Sieko

DuPont Kinston Plant (NC)
Map of Impacted Area



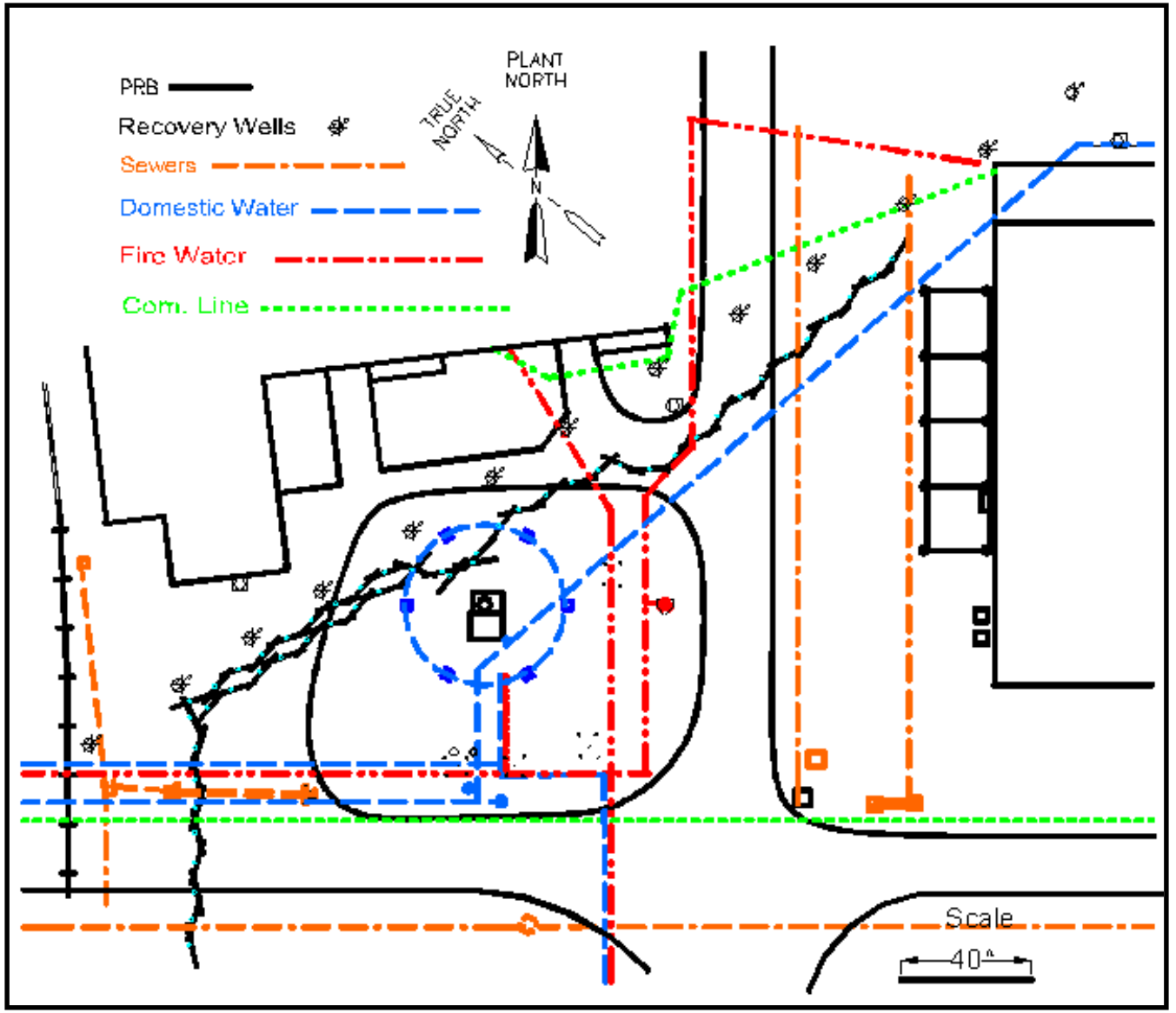
Area of Concern



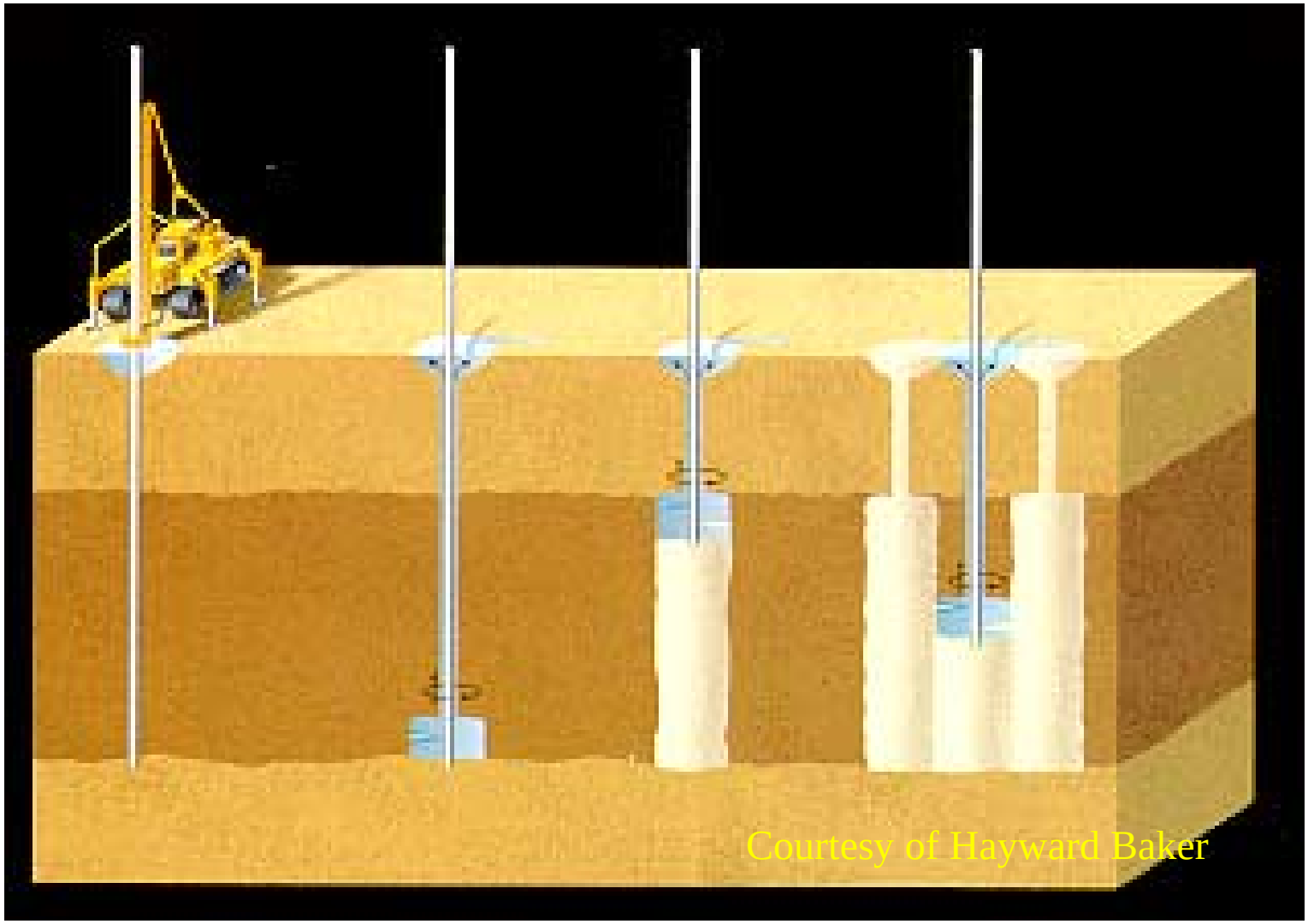
Source Zone Characteristics

- Black, fine-grained, silty sand
- Mudstone confining layer at 15-18 feet.
- Source contained within ~30 foot diameter zone
- TCE concentrations: 25-50 ppm ave; 99 ppm max
- Linear groundwater velocity: 0.05 to 0.1 ft/day
- Plume size: 250-300 ft wide at 300 ft downgradient
- Plume concentrations: 5-2000 ppb

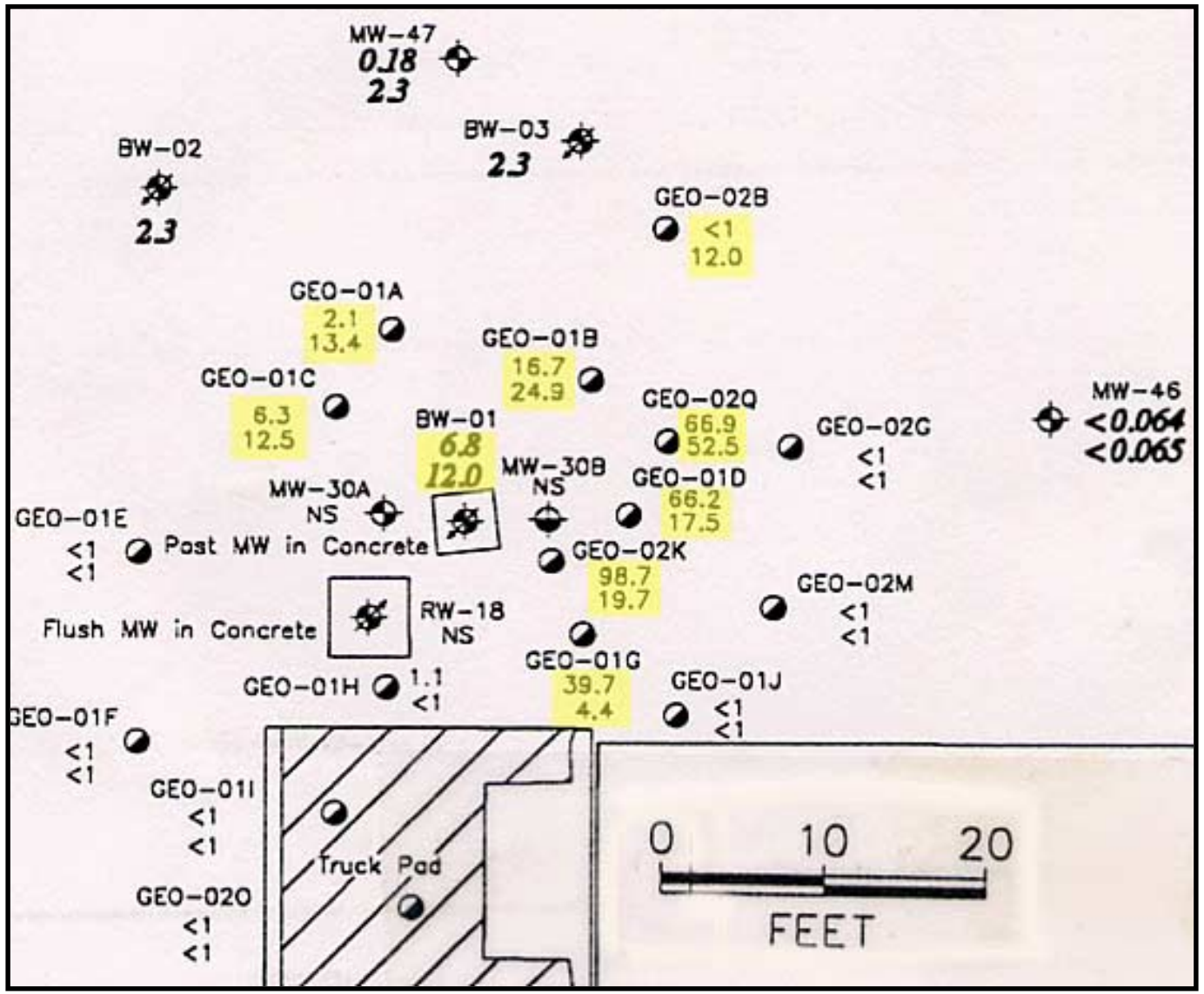
PRB To Treat TCE Plume



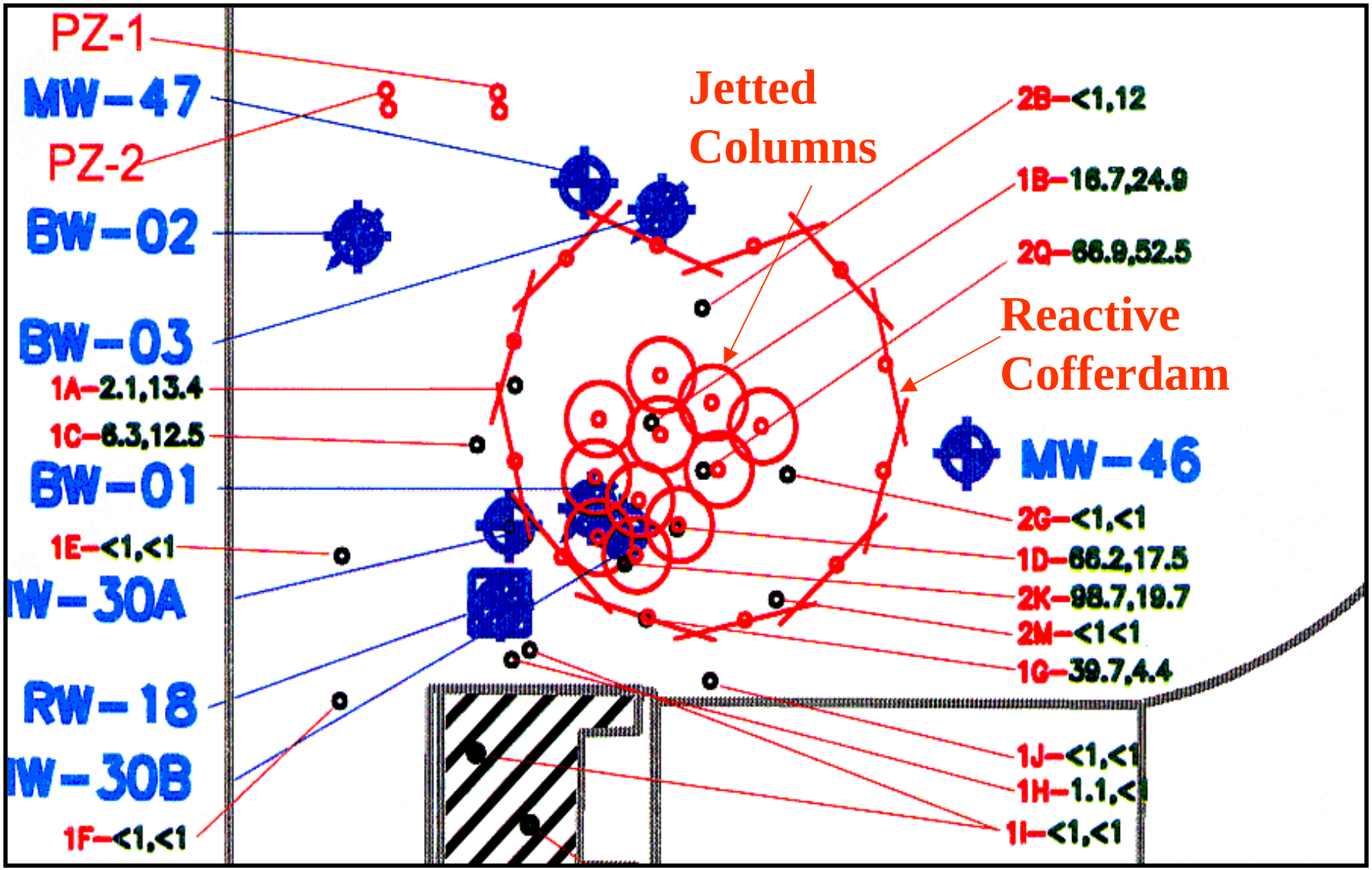
Jetting Process



Source Zone Concentration Map



Source Zone Concentration Map

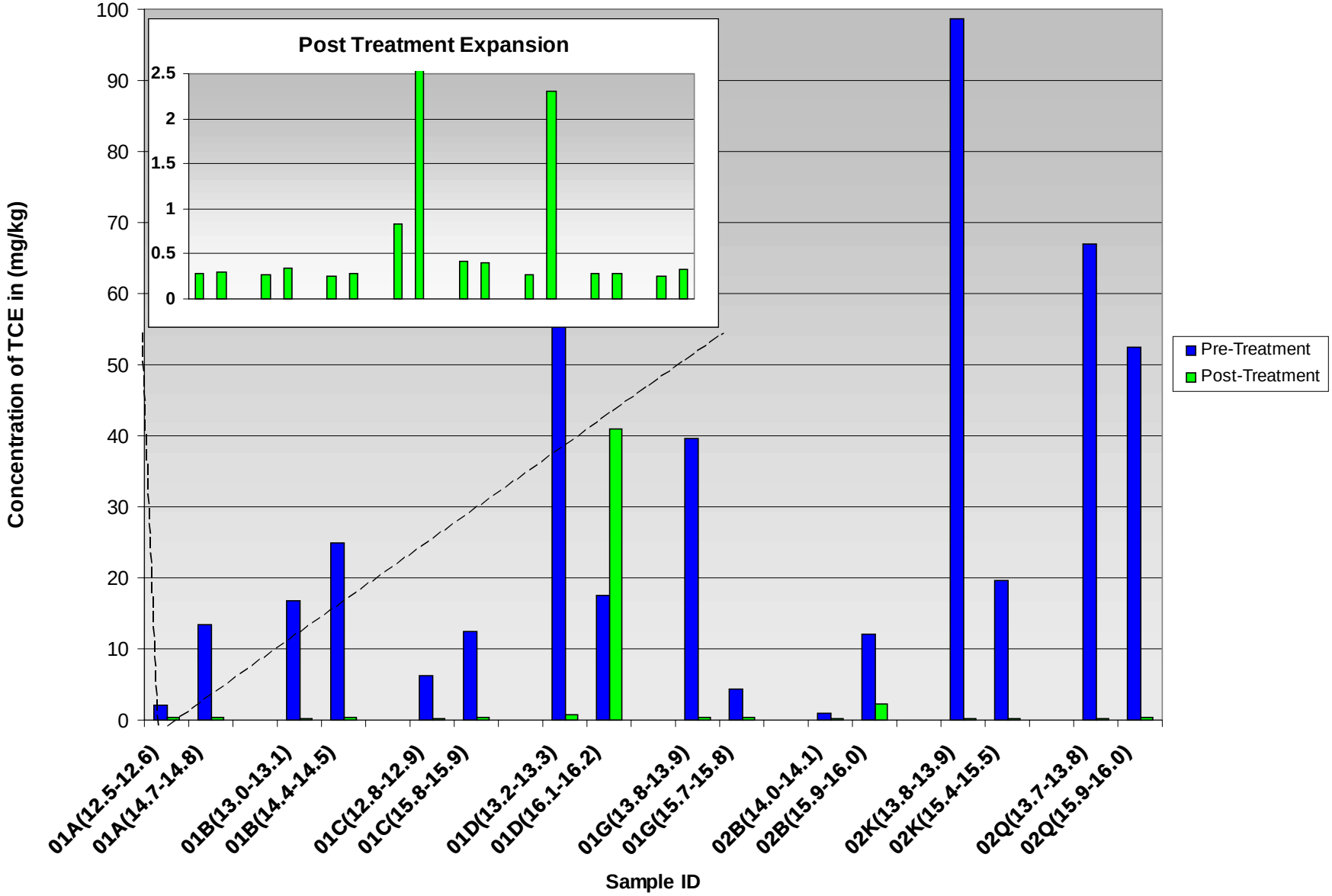


Jetted ZVI Column

Source Zone Jetting Parameters

- Contractor: Hayward-Baker, Baltimore, MD
- 95% kaolinite clay d.w.
- 5% Peerless ZVI (<50 mesh) d.w.
- Number of treatment columns: 11
- Column depths: 15-18 feet
- Treatment column diameter: 5-6 feet
- Column centerline distance: 4-5 feet
- Jetted low K reactive wall cofferdam
- Cofferdam jetting centers: 9 feet

Treatment Compasion of Source Zone Analytical Results



Source Treatment Conclusions

- Lab tests demonstrate ZVI can effectively destroy high concentrations of CT and TCE
- Expect continued growth in use of ZVI technology to treat chlorinated solvents because:
  - It works!
  - Usually a significant cost advantage
  - In-situ, passive treatment is advantageous for site redevelopment and re-use
  - Reliable, robust technology

Resources on the Web

- Oregon Graduate Institute
  - cgr.ese.ogo.edu.iron/
- Envirometal Technologies, Inc.
  - www.eti.ca/eti.html
- EPA
  - www.epa.gov/tio
- RTDF
  - www.rtdf.org

Source Control at the Former Acid Disposal Area

Site Location

Martinsville — Site Description

- Piedmont region of south central Virginia
- Situated within a stream meander of Smith River
- Covers approximately 550 acres
- Over 200 feet of topographic relief

Martinsville — Operational Status

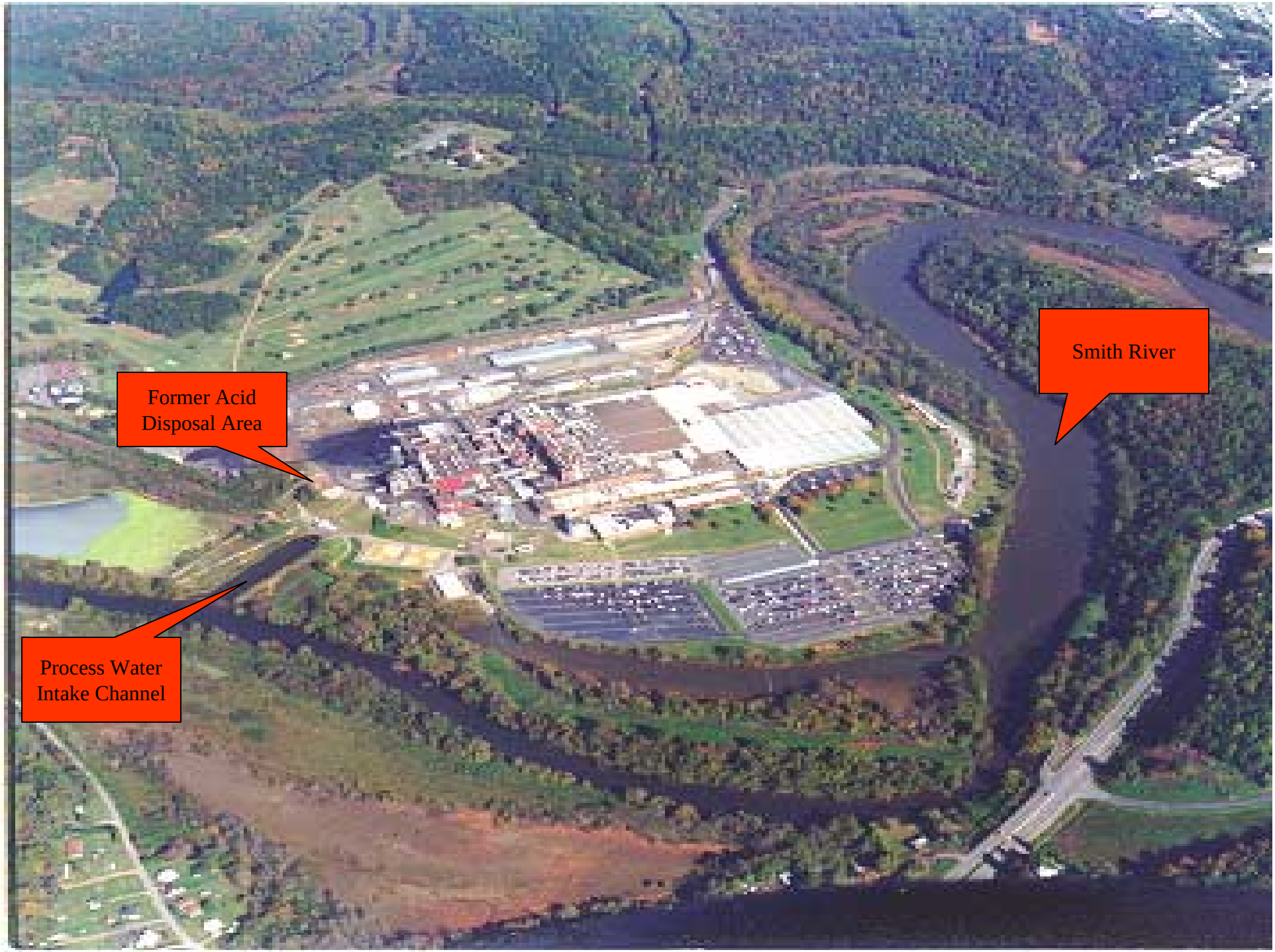
- Nylon operation started 1941
- Manufacturing ceased on June 30, 1998
- Spinnerets fabrication is currently the only DuPont operation on-site

Community Issues

- DuPont was the largest local employer
- Several other textile plant closings / relos
- DuPont managed closing better than others
- Made commitments to assist with local economic revitalization

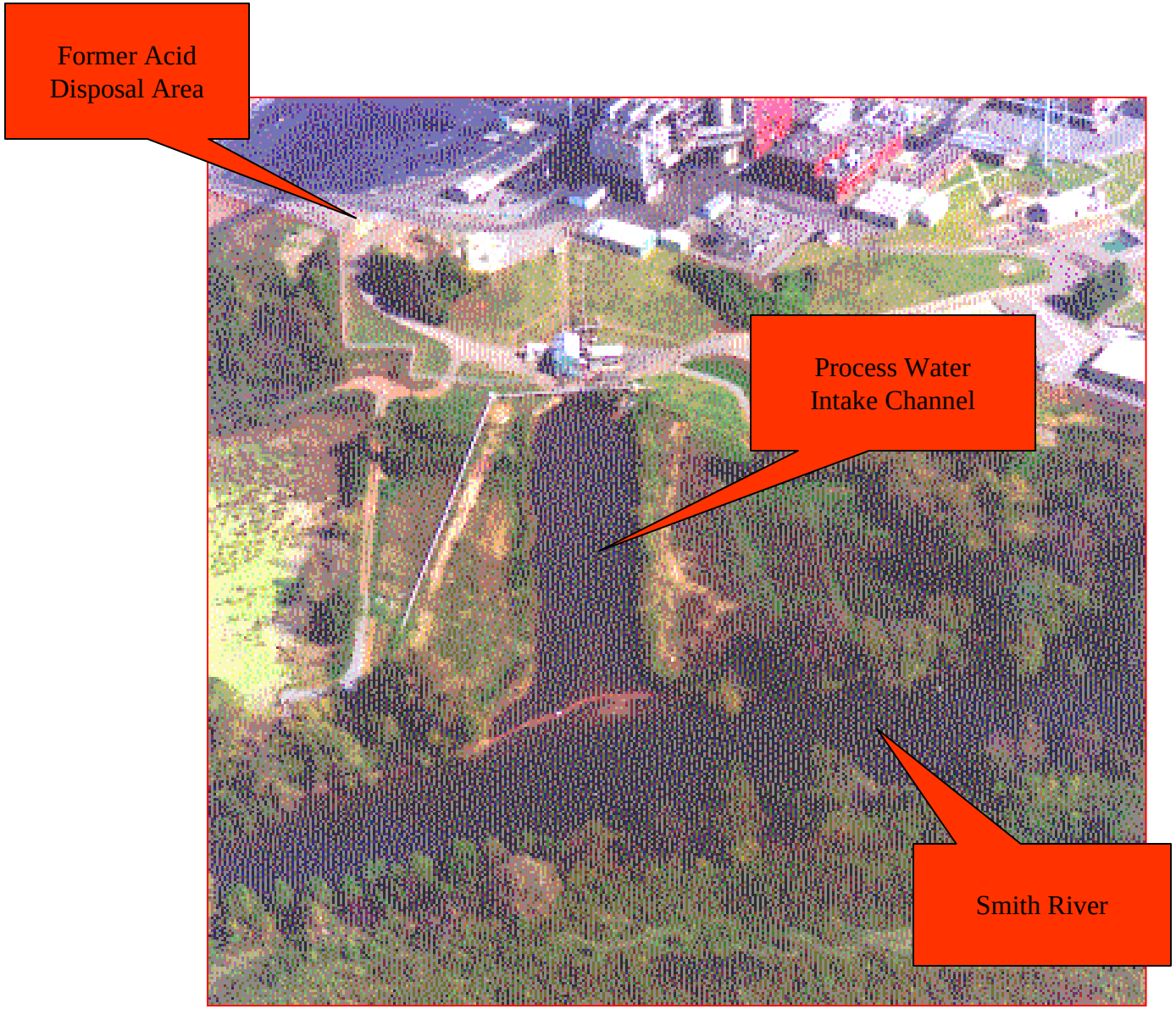
Future Site Plans

- Former nylon manufacturing facilities currently undergoing demolition
- Majority of site to be leased to County for development as a technology park
- No full-time DuPont facility management presence after site is leased to County


Former Acid
Disposal Area
Smith River
Process Water
Intake Channel

Former Acid Disposal Area Description

- Laboratory wastes neutralization pits operated 1958-1974
- An original and replacement pit had concrete walls, open bottom, filled with limestone rocks
- Approximately 5 ft by 10 ft at surface, unknown depth
- Received various laboratory wastes, including spent nitric and formic acids, phenol, carbon tetrachloride (CT)
- Pits were closed by backfilling with soil


Former Acid
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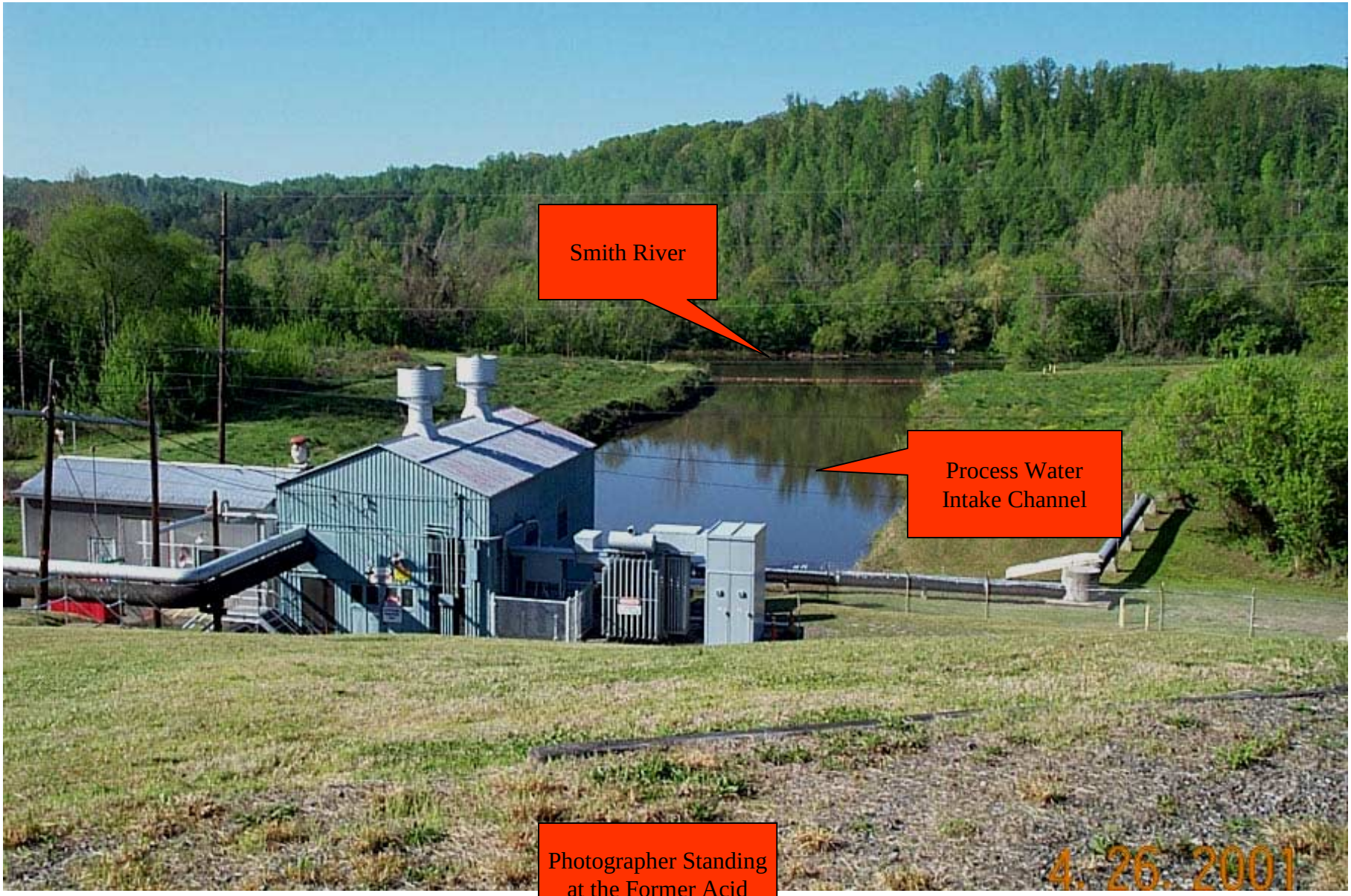
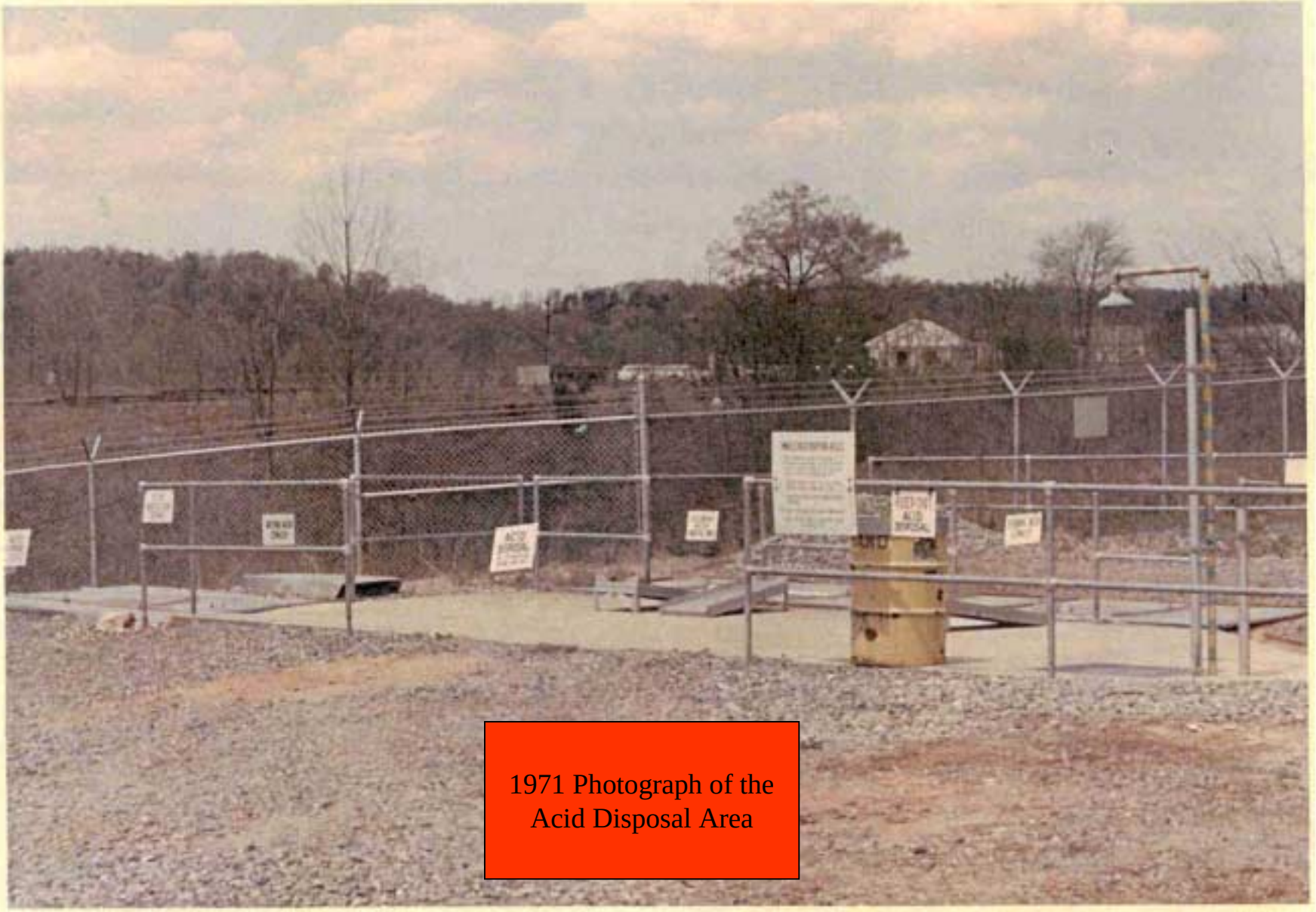


Photographer Standing at the Former Acid Disposal Area



1971 Photograph of the
Acid Disposal Area


CLEANING
ACID
CAUSTIC ONLY


NITRIC ACID

Former Acid Disposal Area
RFI Findings

- Concentrations as high as 30,000 ppm CT in soil
- Approximately 10,000 cubic yards of soil is impacted, very well delineated
- Approximately 20 tons of CT is in the vadose zone (0-25’ bgs)
- Downgradient groundwater and surface water impacts

Groundwater and Surface Water Status

- Smith River is not a drinking water source
- Groundwater is not used for drinking water (public supply)
- Site will continue to be used solely for industrial purposes
- Surface water monitored quarterly at eight locations
- Surface water CT concentrations are very localized
- Indications of an upward trend in surface water CT concentrations
- Indications that CT groundwater plume is not stable

Decision-Making Objectives for the Former Acid Disposal Area

"Concern"	Objective
• Positive EI determinations, and regulatory relationships	• Control off-site migration of COC's
• Good stewardship of remediation budgets	• Select a cost-effective alternative that protects HH&E
• Reduce liability	• Reduce COC discharges to eliminate future liability
• Permanent remedy - no future site presence	• Choose an alternative with long-term effectiveness and no O&M
• Implement remediation safely	• Choose an alternative with acceptable safety/health attributes
• Avoid public relations issues	• Reduce COC discharges enough to prevent negative public image

Management Options

- Continued monitoring of groundwater and surface water
- Downgradient control / treatment of plume
- Contaminant source control

Options Analysis Matrix

	Financial	Regulatory	Public Relations	Liability	Technical	Safety	
General Objectives:	Cost effective, protective of HH&E	Control off-site COC migration, plume stability	Maintain positive relationships	Eliminate / minimize	Long-term effectiveness, no O&M	Minimize H&S exposure	Scoring Results
Option A	5	1	1	1	1	5	14
Monitoring		Does not control migration or stability	May be viewed as not responsive to problem	No immediate impact, liability may increase	Not effective in reducing mobility, toxicity or volume	Minimal exposure	
Option B	1	4	5	5	3	3	21
Downgradient Control		Plume migration control, may not control stability	Highly visible, may have postive short-term results	Positive impact, off-site migration is curtailed	Reduces mobility, toxicity, not volume	Some exposure during installation and operation	
Option C	4	5	4	3	5	3	24
Source Control		May have longer-term effect on migration and stability	Highly visible, results may be longer-term	Longer-term, positive impact on liability	Reduces mobility, toxicity and volume	Some exposure during installation and operation	

* Note: Scale is based on 5 to 1, where 5 is the most positive impact on each category while a 1 represents the most negative impact.

Reasons for Choosing Source Control

- Source area is relatively small and well-defined
- Source control may be effective in controlling migration and plume growth, stabilized plume is necessary to meet EI750
- Fits with plans for future site use, no O&M requirements, cost effective

Source Control Alternatives that Passed the Initial Screening

- Excavation with off-site incineration
- Containment through capping
- Soil vapor extraction (SVE) with off-gas treatment
- In-situ contaminant destruction through zero-valent iron (ZVI) saturation

Remedial Alternatives Analysis Matrix

	Financial	Regulatory	Public Relations	Liability	Technical	Safety	
General Objectives:	Cost effective, protective of HH&E	Control COC migration, plume stability	Maintain positive relationships	Eliminate / minimize	Constructability, Long-term effectiveness, No O&M	Minimize H&S exposure	Scoring Results
Option A	1	5	4	5	3	1	19
Excavate and incinerate		Total removal of COC	Hauling issues, preference for permanent remedy	Permanent removal of material	Constructability issues; no O/M	Much exposure to COC's	
Option B	5	2	2	2	3	5	19
Containment by capping		COC remains untreated, migration may be controlled	Not perceived as a final solution	Minimum reduction in liability	Some on-going maintenance	Minimal exposuures	
Option C	3	3	5	4	3	4	22
Soil vapor extraction		No assurance that all COC's are removed	No impact in community	Mass reduction and assoc. liability reduction	Some effectiveness questions, some on-going O/M	Potential exposures to vapors, condensate	
Option D	4	4	5	4	4	3	24
Zero-valent iron treatment		COC's are treated or contained	No impact in community	Mass reduction and assoc. liability reduction	Minimal on-going maintenance	Potential exposure during mixing	

* Note: Scale is based on 5 to 1, where 5 is the most positive impact on each category while a 1 represents the most negative impact.

Martinsville ZVI Test Area

Equipment Used

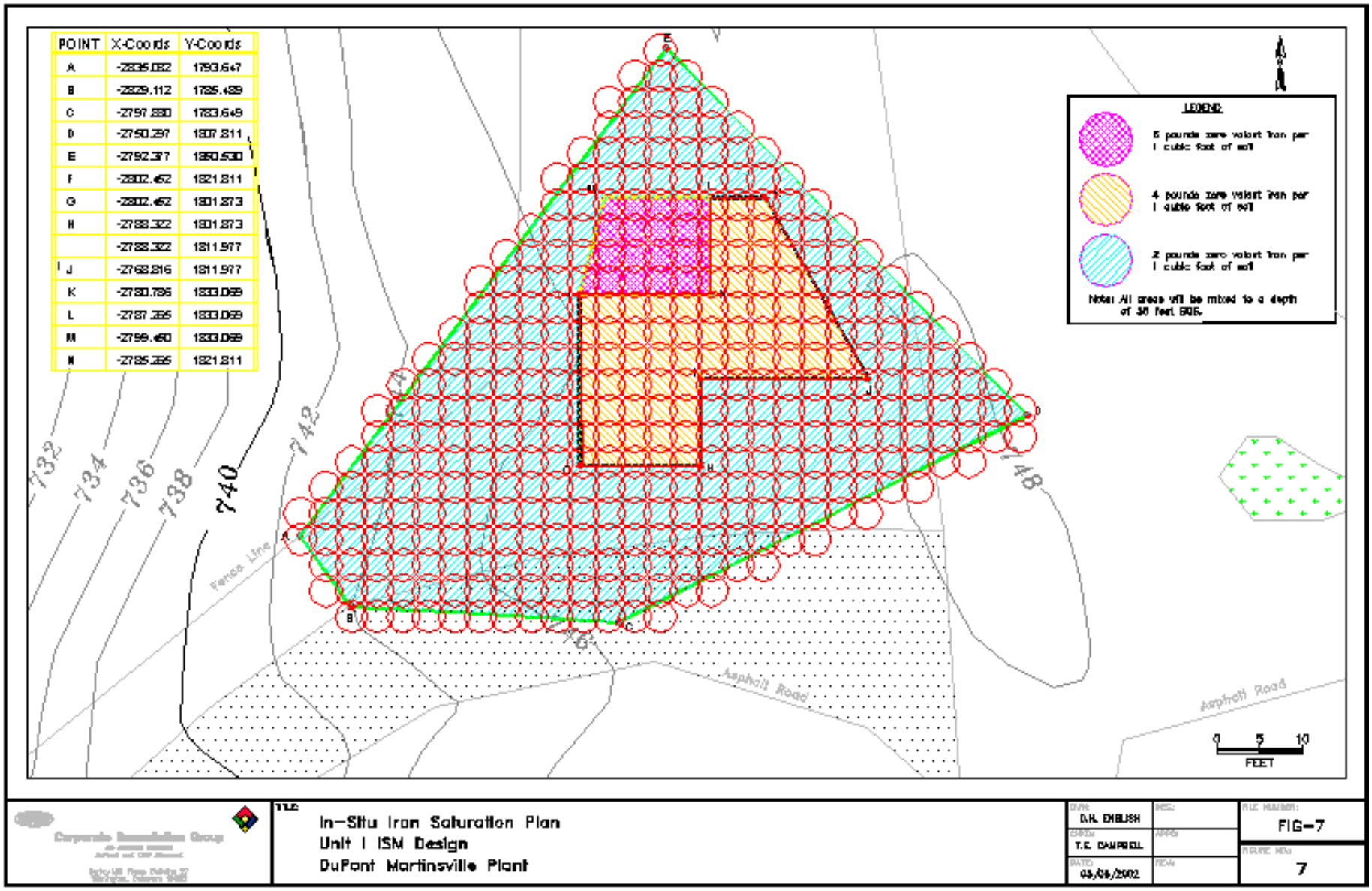
The ZVI and Clay Mix

Injecting ZVI Mix

Injecting ZVI Mix

Contractor Selection for the Martinsville IRM

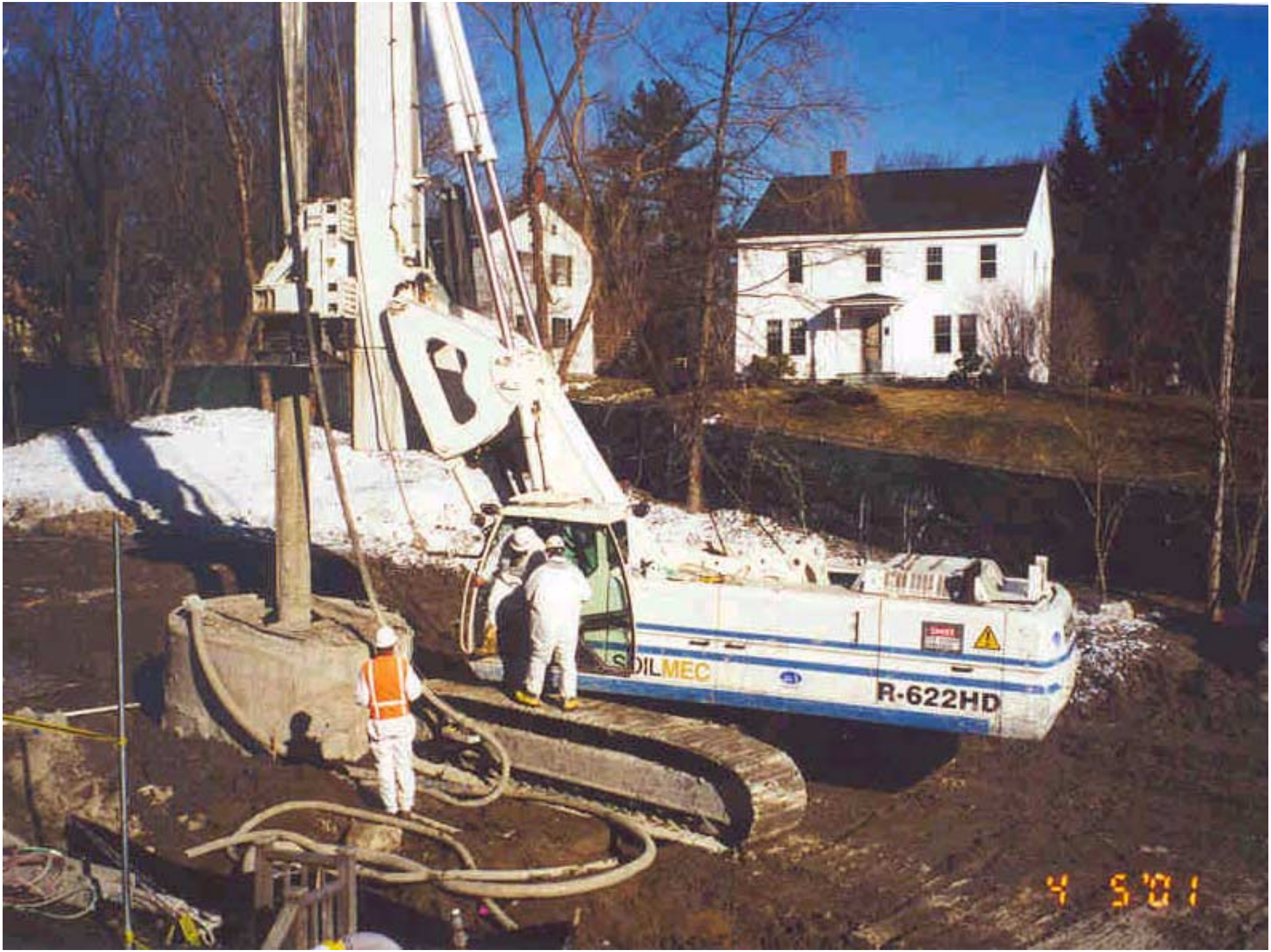
- Competitive Bid
  - GeoCon
  - Recon
  - Sevenson
  - URS Corp
- GeoCon (Monroeville, PA) was selected



Corporate Remediation Group

TITLE:
In-Situ Iron Saturation Plan
Unit I ISM Design
DuPont Martinsville Plant

DWN: D.H. ENGLISH	REC:	FILE NUMBER: FIG-7
CHKD: T.C. CAMPBELL	APPR:	
DATE: 03/08/2002	REVN:	FIGURE NO: 7


SOILMEC
R-622HD

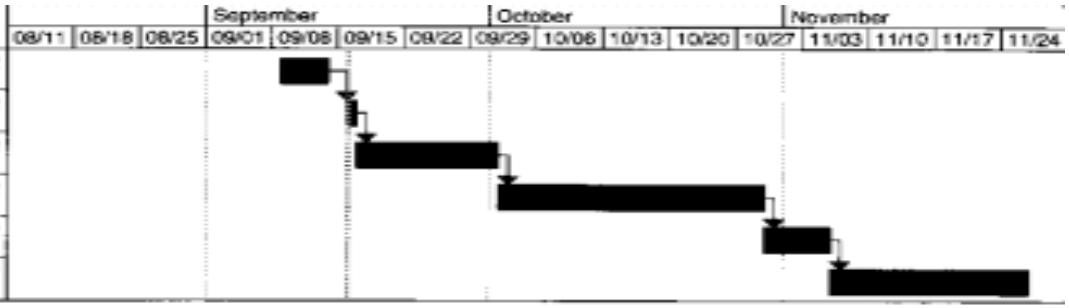

R-622

Project QA/QC Parameters

- Iron and clay content of additive
- Post-mixing soil iron and clay content at various depths
- Post-project soil COC at various depths
- Long-term downgradient groundwater and surface water monitoring program

Construction Schedule

ID	Task Name	Duration	Start	Finish
1	Mobilization	5 days	Mon 09/09/02	Fri 09/13/02
2	Abandon Monitor Wells	1 day	Mon 09/16/02	Mon 09/16/02
3	Remove Utilities & Concrete	11 days	Tue 09/17/02	Tue 10/01/02
4	InSitu Mixing	20 days	Wed 10/02/02	Tue 10/29/02
5	Asphalt cap	5 days	Wed 10/30/02	Tue 11/05/02
6	Demobe & Project Closeout	15 days	Wed 11/06/02	Tue 11/26/02



THANK YOU